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Maize grain and soil surveys reveal suboptimal dietary selenium intake is widespread in Malawi

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Selenium is an essential element in human diets but the risk of suboptimal intake increases where food choices are narrow. Here we show that suboptimal dietary intake (i.e. 20–30 μg Se person^{-1} d^{-1}) is widespread in Malawi, based on a spatial integration of Se concentrations of maize (*Zea mays* L.) grain and soil surveys for 88 field sites, representing 10 primary soil types and >75% of the national land area. The median maize grain Se concentration was 0.019 mg kg^{-1} (range 0.005–0.533), a mean intake of 6.7 μg Se person^{-1} d^{-1} from maize flour based on national consumption patterns. Maize grain Se concentration was up to 10-fold higher in crops grown on soils with naturally high pH (>6.5) (Eutric Vertisols). Under these less acidic conditions, Se becomes considerably more available to plants due to the greater solubility of Se$^{(IV)}$ species and oxidation to Se$^{(VI)}$.

Selenium (Se) is an essential element for humans and livestock. A total of 25 genes encoding selenoproteins have been identified in humans, including iodothyronine deiodinases, thioredoxin reductases, glutathione peroxidases, and a range of other selenoproteins (e.g. SelP, SelM, SelT)[1]. These proteins have critical roles in thyroid functioning, cell proliferation and survival through redox homeostasis, antioxidant defence and the immune response. When Se intake is suboptimal, the selenoprotein status of people decreases and there are increased risks of adverse health effects. At extremely low Se intake levels (where habitual intakes for adults are <20 μg Se d^{-1}), clinical deficiency disorders have been reported including Keshan disease (a cardiomyopathy) and Kashin-Beck disease (an osteoarthropathy). Where habitual intakes for adults are less than those needed for maximal expression of glutathione peroxidase, typically at least 40 μg Se d^{-1}, there is an increased risk of health disorders, including cardiovascular disorders, impaired immune functions, and some cancers[1]. The relationships between Se intake, Se status in terms of selenoprotein expression and health outcomes have still to be fully resolved[2,3]. These uncertainties are reflected in the wide range of Dietary Reference Intake (DRI) levels in different countries[1]. Some DRIs are set to reduce risks of overt deficiency (i.e. recommending intakes of ~40 μg Se d^{-1}), although most countries have recommended intake levels of 50–70 μg Se d^{-1}. As high habitual levels of Se intake are potentially toxic (>400–900 μg Se d^{-1}), care must be taken in setting DRIs and recommending dietary supplementation.

Selenium intake in human populations is derived primarily from dietary sources and can be determined from direct dietary analyses or surveys and food composition tables. Reported Se intakes range from 3 to 7000 μg Se d^{-1} globally[4] due to differing dietary preferences and the levels of plant available Se in the soil on which crops are grown for consumption[1,4–7]. Populations in many European countries and elsewhere have intakes <50 μg Se d^{-1}, which are likely to be suboptimal in terms of selenoprotein expression[2]. Higher dietary Se intake levels (>150 μg Se d^{-1}) occur in Se-rich (seleniferous) environments (e.g. parts of China, India, North America, and Venezuela) and where seafood-based diets containing high concentrations of Se are prevalent (e.g. notably in parts of Greenland and Japan). Selenium intake from water and air is usually insignificant, except where environmental Se concentrations are high due to natural or anthropogenic factors[4].

The extent of Se deficiency in human populations is unclear, although it is likely to be widespread in global terms and especially where food choices are narrow. For example, surveys of Se concentrations in rice grain show that Se intake is likely to be suboptimal in many populations reliant on a staple diet of rice[8]. In Sub-Saharan Africa

(SSA), Se intake levels are often very low in rural populations where fish consumption is limited. Thus, in rural Burundi, intakes of 17 µg Se d[−1] have been reported in adults[9]. In southern Malawi, intakes of 15–21 µg Se d[−1] have been reported among children living in rural areas of Zomba District[10], consistent with low blood plasma Se concentrations (<55 µg L^{−1}) among adults in the same area[11,12]. A substantial proportion of dietary Se intake in SSA has been attributed to fish consumption[10,13]. Indeed, higher Se intakes (44–46 µg Se d[−1]) have been reported in Mangochi District, adjacent to the southern end of Lake Malawi, where fish consumption is likely to be high[14]. In Burundi, higher Se intakes have also been reported in middle-class men (82 µg Se d[−1]) and mothers (38 µg Se d[−1]), which have been linked to variation in fish consumption between groups[9].

In rural SSA, maize grain is the dominant staple food. In Malawi (mean energy intake 2172 kcal person[−1] d^{−1}) and neighbouring Zambia (1873 kcal person[−1] d^{−1}), ~52% of total dietary calorie intake is derived from maize (2007 data; ref 15). This equates to 0.354 and 0.315 kg person d[−1] in Malawi and Zambia, respectively. Consumption of animal products from all sources (meat, offal, fats, milk and eggs) is typically low, accounting for 64 and 97 kcal person[−1] d^{−1} in Malawi and Zambia, respectively, of which fish accounts for 9 and 11 kcal person[−1] d^{−1}. Maize grain is therefore likely to be critical in determining Se intakes to the average SSA diet despite being low in terms of Se concentration according to local food composition tables. For example, in Malawi, whole-grain maize flour

contained 25 µg Se kg^{−1} in Zomba District[13] and 49 µg Se kg^{−1} in Mangochi District[16].

This study aimed to determine the contribution of maize grain to dietary Se intake in rural Malawi and establish whether maize grain Se concentration is dependent on soil Se concentration and/or other soil factors (e.g. pH, organic matter content). Malawi was chosen because: (1) a large proportion of the population engages in subsistence farming and their diets are dominated by maize; (2) dietary Se intakes and Se status are likely to be low among rural populations[10–13]; (3) there is a high national prevalence of immunological disorders (e.g. HIV/AIDS) and other morbidity symptoms which are associated with low micronutrient status[1,17,18]; (4) the national government operates a national Farm Input Subsidy Programme[19] which provides the opportunity to consider agronomic biofortification *via* incorporation of trace quantities of Se in compound fertilisers. Such a strategy to alleviate suboptimal dietary Se intakes was adopted at a national scale in Finland in 1984 and is feasible in other contexts[20–22].

Results

Estimating Se intake from dietary sources in Malawi using published data. National food consumption patterns and published Se concentration data for food were used to estimate baseline Se intakes for two Districts in rural Malawi. Mean dietary Se intakes of 39.8 and 24.4 µg Se person[−1] d^{−1} were estimated for Mangochi and Zomba Districts, respectively, with Se intake from all non-maize sources being 22.4 and 15.5 µg Se person[−1] d^{−1}, respectively (Table 1).

Table 1 | Average daily food supply and Se intake in two areas of Malawi, Mangochi and Zomba Districts (based on refs 13, 15, 16)

Foodstuff	Supply per capita[a] (g d^{−1})	Supply per capita[a] (kcal d[−1])	Eick (2007; ref. 16)	Eick (2007; ref. 16) Notes/sources	Donovan et al. (1991; ref. 13)	Donovan et al. (1991; ref. 13) Notes/sources	Se intake (µg person[−1] d^{−1}) Mangochi	Se intake (µg person[−1] d^{−1}) Zomba
Maize	354	1126	49	''whole-grain flour''	25	unrefined, unfermented	17.36	8.86
Potatoes	275	192	2		2	n.d., use Eick (2007)	0.55	0.55
Cassava	197	136	2	no data (n.d.), assume ≈ potato	2	n.d., use Eick (2007)	0.39	0.39
Wheat	17	49	79		79	n.d., use Eick (2007)	1.34	1.34
Rice (milled equivalent)	12	44	10		24		0.12	0.30
Sorghum	6	19	84		129	unmilled	0.48	0.74
Millet	6	18	84	n.d., assume ≈ sorghum	80	milled	0.48	0.46
Sugar (Raw equivalent)	33	117	0	n.d., assume zero	0	n.d., assume zero	0.00	0.00
Beans	13	44	22	''kidney bean''	7	''kidney bean''	0.29	0.09
Pulses, other	23	81	159	''pigeon pea'' (155), ''cowpea'' (163)	60	''pigeon pea'' (56), (64)	3.70	1.40
Groundnuts (shelled equivalent)	13	66	94	dry average (74, 113)	94	n.d., use Eick (2007)	1.20	1.20
Vegetable oils	7	62	0	n.d., assume zero	0	n.d., use Eick (2007)	0.00	0.00
Tomatoes	7	1	9	fresh average (10, 8)	9	n.d., use Eick (2007)	0.06	0.06
Onions	10	4	33	''white'' (11) & ''red'' (54) onions	33	n.d., use Eick (2007)	0.33	0.33
Vegetables, other	42	9	36	''ch. cbge'' (2), ''pumpkin lvs'' (70)	7	''Amaranthus, okra, c'sava lvs'' (7)	1.51	0.29
Bananas	67	40	9		5		0.60	0.33
Plantains	56	50	9	assume ≈ banana	5	assume ≈ banana	0.51	0.28
Fruits, other	46	20	27	''mango''	4	''mango'' average (3, 3, 6)	1.24	0.18
Beverages, fermented	41	14	4	''thobwa gruel''	4	n.d., use Eick (2007)	0.16	0.16
Bovine meat	5	10	70	n.d., beef ''raw mince'' (ref. 33)	70	n.d., beef ''raw mince'' (ref. 33)	0.35	0.35
Mutton & goat meat	4	5	20	n.d., lamb ''raw mince'' (ref. 33)	20	n.d., lamb ''raw mince'' (ref. 33)	0.07	0.07
Pig meat	5	19	140	n.d., pork ''raw mince'' (ref. 33)	140	n.d., pork ''raw mince'' (ref. 33)	0.65	0.65
Poultry meat	3	4	130	n.d., chicken ''meat only'' (ref. 33)	130	n.d., chicken ''meat only'' (ref. 33)	0.39	0.39
Eggs	3	4	15	''chicken egg''	20	''duck egg''	0.05	0.06
Milk (excluding butter)	10	6	10	n.d., cow milk data (ref. 38)	10	n.d., cow milk data (ref. 38)	0.09	0.09
Fish & seafood	14	9	574	''smoked fish'', ''usipa'' (305, 842)	420	''smoked chambo'', usipa (108, 732)	7.86	5.75
Sub-total[b]		2149				Average Se intake (all sources)	39.80	24.35
Grand total (all food sources)		2172				Average Se intake (excl. maize)	22.44	15.49

[a]*Per capita* supply in 2007 (FAO, 2011; ref 15) reported as kcal (1 kcal = 4.19 kJ). Data represent means, calculated from total supply available for consumption, divided by total population living within the national borders. Actual intake is likely to be lower due to losses during storage, preparation and cooking. Energy values based on typically consumed crop fractions.
[b]Some minor food groups excluded in this table, although 98.9% of energy intake is represented.

Thus, maize was the single major foodstuff contributing to dietary Se intake. As food consumption data are based on national *per capita* supplies which will overestimate food intake due to food wastage during storage, preparation and cooking[15], Se intakes are likely to be lower than these estimated values.

The use of a single national food consumption metric masks substantial within-country variation in Se intake due to differing food consumption patterns. For example, fish consumption is likely to be higher in Mangochi, near Lake Malawi, than in Zomba District. A median Se intake of 45 µg person^{-1} d^{-1} (interquartile range=30) for Mangochi District was reported by Eick et al.[14], based largely on the same food composition data, using dietary recall surveys and questionnaires. Adult Se intake was not reported for Zomba District[10], but Se intake by children aged 4–6 ranged from 15–20 µg person d^{-1}. The link between fish consumption and dietary Se intake has previously been associated with income levels in Burundi[9]. The higher dietary Se intake estimate at Mangochi compared to Zomba in the present analysis reflects differences in the Se concentration of edible crop portions reported by Donovan et al.[13] and Eick[16]. For example, the Se concentration of whole-grain maize flour was 49 µg Se kg^{-1} in Mangochi compared to 25 µg Se kg^{-1} in Zomba. If food consumption patterns were identical in both Districts, maize would account for 46% and 36% of dietary Se intake in Mangochi and Zomba, respectively. In addition, the Se concentration of mango, banana, pigeon pea, and kidney bean was ~2–6-fold higher in Mangochi than in Zomba. Assuming there were no systematic differences in sample collection, preparation or analysis between Donovan et al.[13] and Eick[16], these consistent differences in crop Se concentration between Districts probably result from soil factors rather than cultivar differences[20–23]. However, the combined Se intake from fruit, vegetables, other cereals and starchy staples was still less than that from maize in both Mangochi and Zomba. Selenium intake from animal sources other than fish is likely to be low, based on the limited contribution of these food sources to the typical Malawian diet. However, as there are gaps in Se concentration data for these categories in local food composition tables, this conclusion requires further validation.

Variation in the Se concentration of maize grain in Malawi. To determine the wider contribution of maize grain to dietary Se intakes in Malawi, samples of soil and grain were collected nationwide (Fig. 1). In 2009, Se concentration in maize grain from 73 sites ranged from 0.0045 to 0.533 mg Se kg^{-1} with a median value of 0.016 mg Se kg^{-1}; over 70% of the samples had a lower Se
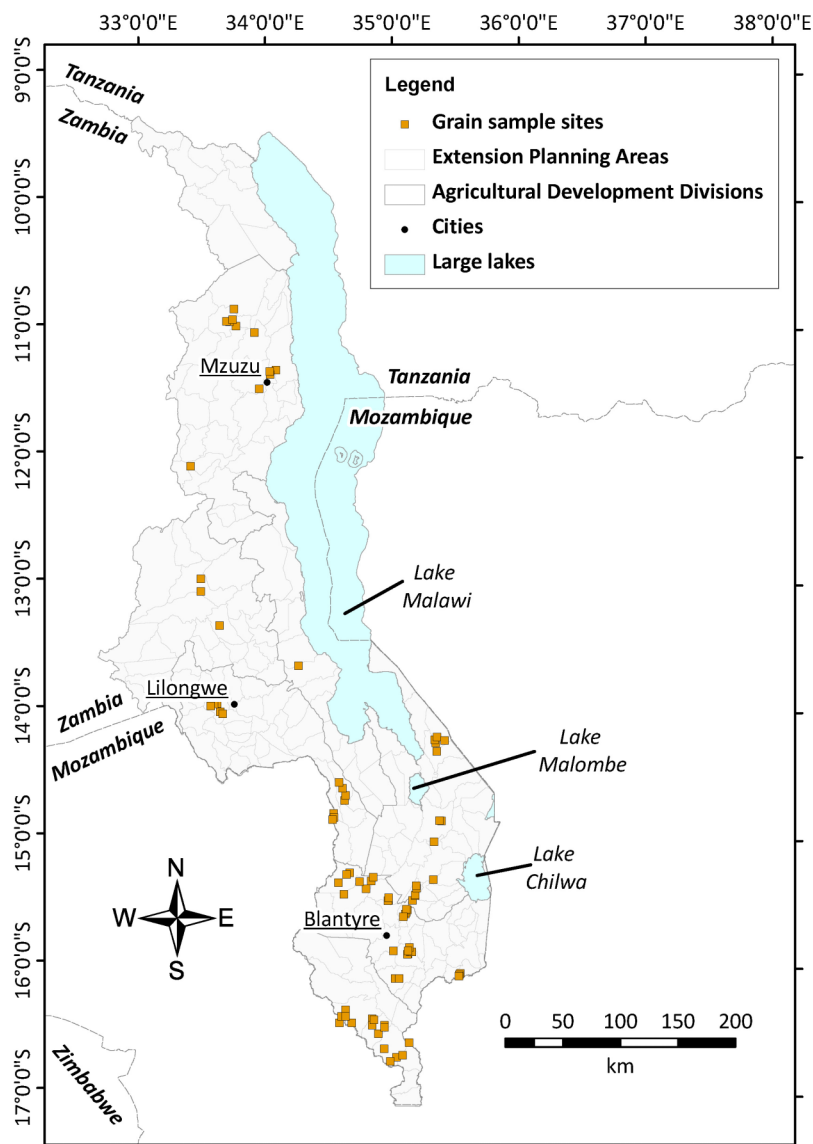

Figure 1 | Location of farmers' fields sampling sites in Malawi produced using ArcGIS (v. 9.3).

concentrations than reported by Donovan et al.[13]. However, there was a disjunct distribution of grain Se concentrations as 69 samples contained <0.08 mg Se kg^{-1} whereas one sample from Lisungwi EPA contained 0.146 mg Se kg^{-1} and another from Mikalango EPA contained 0.533 mg Se kg^{-1}. The sample from Mikalango was from a crop growing on a Eutric Vertisol[24] with a pH of 7.9. Therefore, in 2010, a further 15 samples were collected from other Shire Valley Eutric Vertisol sites in the Mangoti, Dolo and Mikalango EPAs with soil pH values ranging from 6.97–8.02. In 2010, grain Se ranged from 0.173–0.413 mg Se kg^{-1} for 13 of the sites, although two sites in Mangoti had lower concentrations of 0.0054 mg Se kg^{-1}.

Mean grain Se concentrations expressed on an EPA basis are presented, in ascending order, in Figure 2a. Based on a mean *per capita* consumption of 0.354 kg d^{-1} and an overall median grain Se concentration of 0.019 mg Se kg^{-1} from all 88 sites, the estimated median Se intake from maize is 6.7 µg Se person^{-1} d^{-1} (range 1.6 to 189).

Soil factors affect maize grain Se concentration. Mean and median total soil Se concentrations were 0.1941 and 0.1623 mg Se kg^{-1}, respectively and there was ~12-fold variation in values between 0.0521 and 0.6195 mg Se kg^{-1}. Mean and median KH$_2$PO$_4$-extractable soil
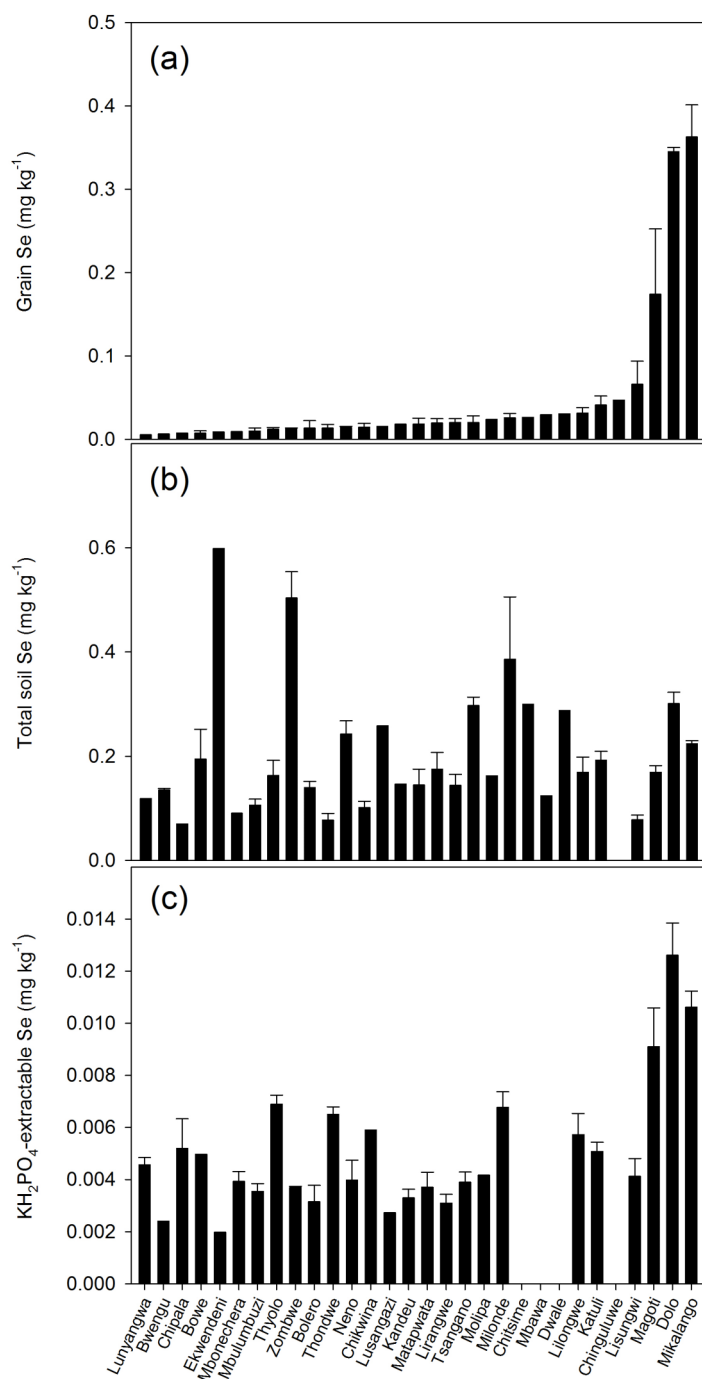

Figure 2 | Concentrations of Se in maize grain (a) and soil (b,c) from farmers' fields surveys in Malawi. Soil Se is expressed as total (b) and KH$_2$PO$_4$-extractable (c) Se forms. Data are presented on an Extension Planning Area (EPA) basis (mean ±s.e.m.). Note, total and KH$_2$PO$_4$-extractable soil Se data are missing for Chinguluwe EPA due to the loss of the soil sample. For Chitsime, Mbawa, and Ntonda EPAs there was insufficient soil sample remaining for KH$_2$PO$_4$-extractable Se to be analysed following other soil analyses.

Se concentrations were 0.0056 and 0.0046 mg Se kg^{-1}, respectively and there was again a ~12-fold variation in values between 0.0013 and 0.0158 mg Se kg^{-1}. There was no obvious link between grain and soil Se concentrations when data were expressed on a mean EPA basis (Fig. 2). Across all sites, there was evidence of a correlation between grain Se concentration and soil pH, especially at pH >6.5 (Fig. 3). There were weaker positive correlations between total soil Se, KH$_2$PO$_4$-extractable Se and soil organic matter. There was also a weak positive correlation between grain Se concentration and KH$_2$PO$_4$-extractable, but not total, soil Se concentration.

Discussion

The use of previously published soil maps and demographic information, new data for maize grain Se concentrations, and geographical information systems (GIS) based approaches clearly showed that dietary Se deficiency is likely to be widespread in Malawi (Figs 4, 5; Table 2). First, the median grain Se concentration for each of the 10 soil types sampled was calculated (Table 2). Second, the area represented by each of the 10 soil types within each District was estimated using ArcGIS (v. 9.3, ESRI, Redlands, CA, USA) using the most recent cartographic data for FAO soil series (ref. 24; Fig. 4, Table 2). By integrating these data, it is possible to predict grain Se concentrations for >75% of the land area in Malawi (Fig. 5; Table 2) and estimate dietary Se intake assuming a mean *per capita* consumption of 0.354 kg maize flour d^{-1}.

Predicted Se intake, adjusted for soil series at a District level, shows that 50% of the population currently consumes <6 µg Se person^{-1} d^{-1}, 75% <7 µg Se person^{-1} d^{-1} and 90% <7.5 µg Se person^{-1} d^{-1} from maize sources (Table 2). Given that Se intake from all non-maize sources is likely to range between 15–22 µg Se person^{-1} d^{-1} (Table 1) and that some groups will obtain a larger proportion of their dietary energy intake from maize, suboptimal Se intake appears to be the norm in Malawi. This extrapolation is based on the major assumption that soil-to-grain transfer is determined primarily by soil properties. Given the critical role of Se in human health, this assumption must now be tested by more detailed sampling and incorporation of other factors such as soil management, dietary choices and biomarkers of Se intake and status among the population, within an appropriate geospatially-informed framework. There is also a pressing need for further sampling of soils and grain in a wider regional and global context to determine the likely scale of suboptimal Se intake, especially among populations reliant on staple cereal crops such as maize. Furthermore, whilst it is likely that the majority of Se in maize grain will be in the form of selenomethionine, as has been found for other cereal grains including rice[25] and wheat[26], this assumption should be tested in future studies to determine the potential bioavailability of Se in human diets, alongside direct measurements of blood Se status and health biomarkers[1].

The marked difference in Se concentration between maize grown on the calcareous Eutric Vertisols of the Shire Valley and almost all
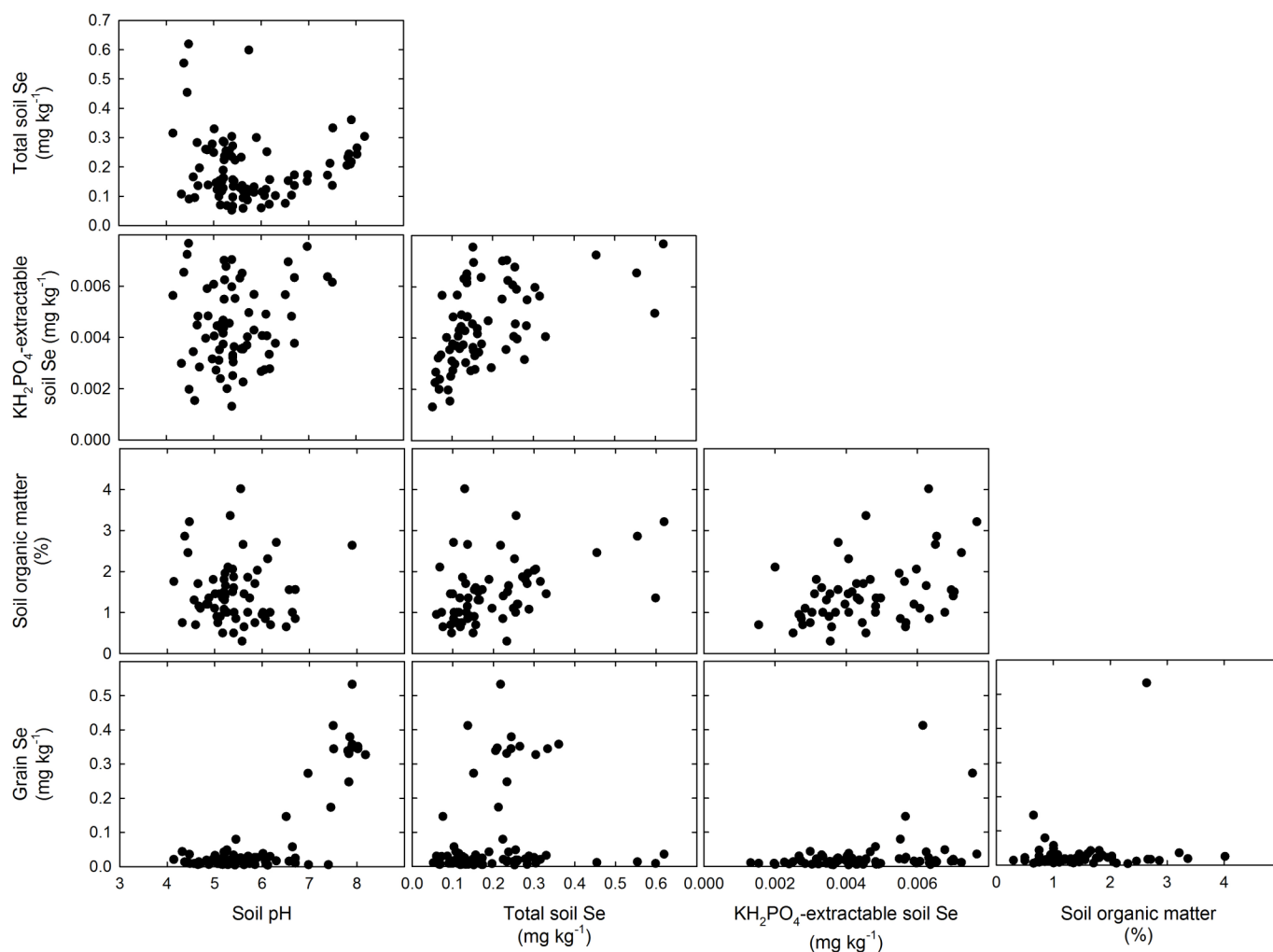

Figure 3 | Relationships between soil Se (total and KH$_2$PO$_4$-extractable forms) and soil pH, soil organic matter and maize grain Se concentration from a survey of farmers' fields in Malawi.
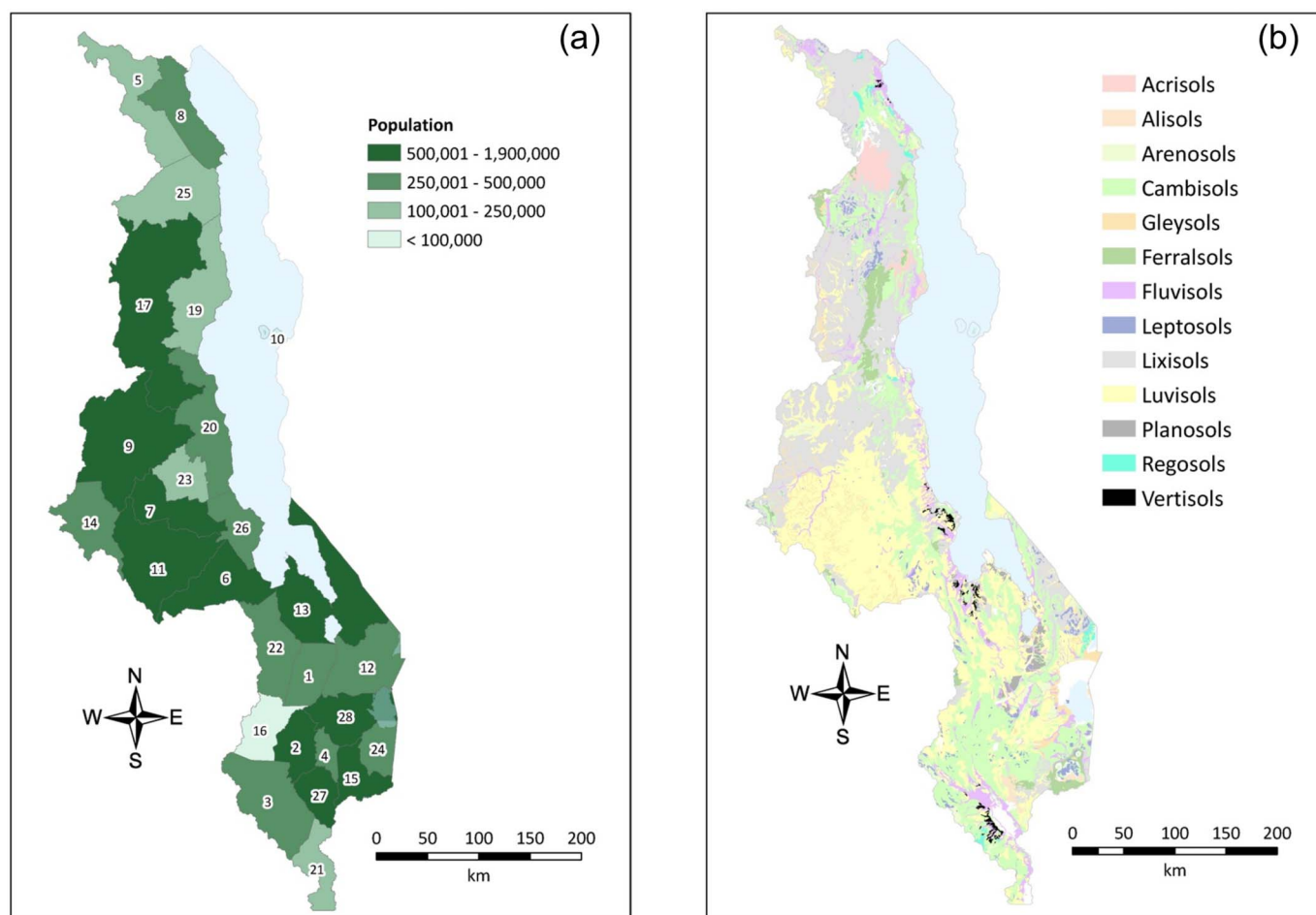
Figure 4 | (a) Population distribution in Malawi at a District level. Districts are numbered #1 (Balaka District) to #28 (Zomba District) as stated in Table 2 (NSO, 2008; ref. 37; N.B. Neno District (#18) maps within Mwanza District (#16) and is not shown), (b) soil series maps based on ref. 24. Figure produced using ArcGIS (v. 9.3).

other soil types in Malawi may arise from a combination of factors, the most obvious being soil pH (Fig. 3) which had a profound influence on Se uptake at pH >6.5 but only a weak correlation in more acidic soils. The pH-dependence of selenate and selenite adsorption on Fe oxides may partly explain this trend. Using Extended X-ray Absorption Fine Structure (EXAFS) data, Peak and Sparks[27] showed that specific bonding (inner-sphere co-ordination) of selenate (Se^{VI}; $pKa_2 = 1.92$) on Fe hydrous oxides declined between pH 3.5 and pH 6. By contrast, selenite (Se^{IV}; $pKa_2 = 7.3$) was specifically adsorbed beyond the 'point of zero charge' of Fe oxides (pH ~7–8), whereas the adsorption envelope of $HSeO_3^-/SeO_3^{2-}$ on haematite shows a marked fall in sorption strength in the pH range 6–8 (ref. 28) as expected from the second pKa value (7.3) of selenious acid[29]. The pH value at which Se uptake increases corresponds closely with the value at which (i) selenate adsorption on Fe oxides ceases and (ii) the selenite sorption envelope declines. An additional factor may be the dependence of inorganic speciation on Eh-pH relations. Thus, it is clear from Eh-pH predominance diagrams[30] and recognised from studies of solubility[31] that selenate is the dominant form of available inorganic Se under oxic and alkaline soil conditions. Other studies of Se solubility and bioavailability have also identified the importance of competition by phosphate ($H_2PO_4^-/HPO_4^{2-}$) for soil adsorption sites[29] and by sulphate (SO_4^{2-}) for root uptake[32], all of which depend on individual soil properties such as pH and mineralogy.

Finally, it must also be recognised that very little soil Se (~3%) exists in a form which is extractable using KH_2PO_4, and that cycling between organic and inorganic forms may influence Se uptake during the growing season. It is also possible that organic-inorganic Se transformations in soils may contribute to the profound differences in Se uptake by maize seen in the Eutric Vertisols of the Shire Valley. Although these soils occupy ~0.5% of the land area of Malawi, it is important to take these and other local variation in soil chemistry into account if agronomic biofortification strategies, such as those previously adopted in Finland, are to be successfully adopted[20–22]. Furthermore, several soil types were not sampled in this study, representing 23% of the land area of Malawi, including 43 and 30% of the land area of Chikwawa and Salima Districts, which contain the greatest area of Eutric Vertisols (Table 2). More detailed geochemical sampling of soil, maize grain, and other crops is now required for Se and other elements. These geochemical data must then be integrated with spatially resolved data on crop production and food choice to support sustainable and safe strategies to alleviate mineral malnutrition in Malawi and the wider region.

Methods

Sourcing pre-existing data to estimate dietary Se intakes. Dietary Se intake in Malawi was estimated from national food consumption data and Se concentration in dietary components. Food consumption data were sourced from the most recent Food and Agriculture Organization (FAO) report (2007; ref. 15). Food Se concentrations for those products contributing the majority of the national average diet in Malawi were taken from Donovan et al.[13] and Eick[16] (Table 1). In Donovan et al.[13], Se concentration was measured in 37 food products collected in rural areas of Zomba District using neutron activation analyses. These data were reported on a fresh weight basis. In Eick[16], Se concentration was measured for 40 food products collected in Mangochi District, near Lake Malawi, using inductively coupled plasma-mass spectrometry (ICP-MS);
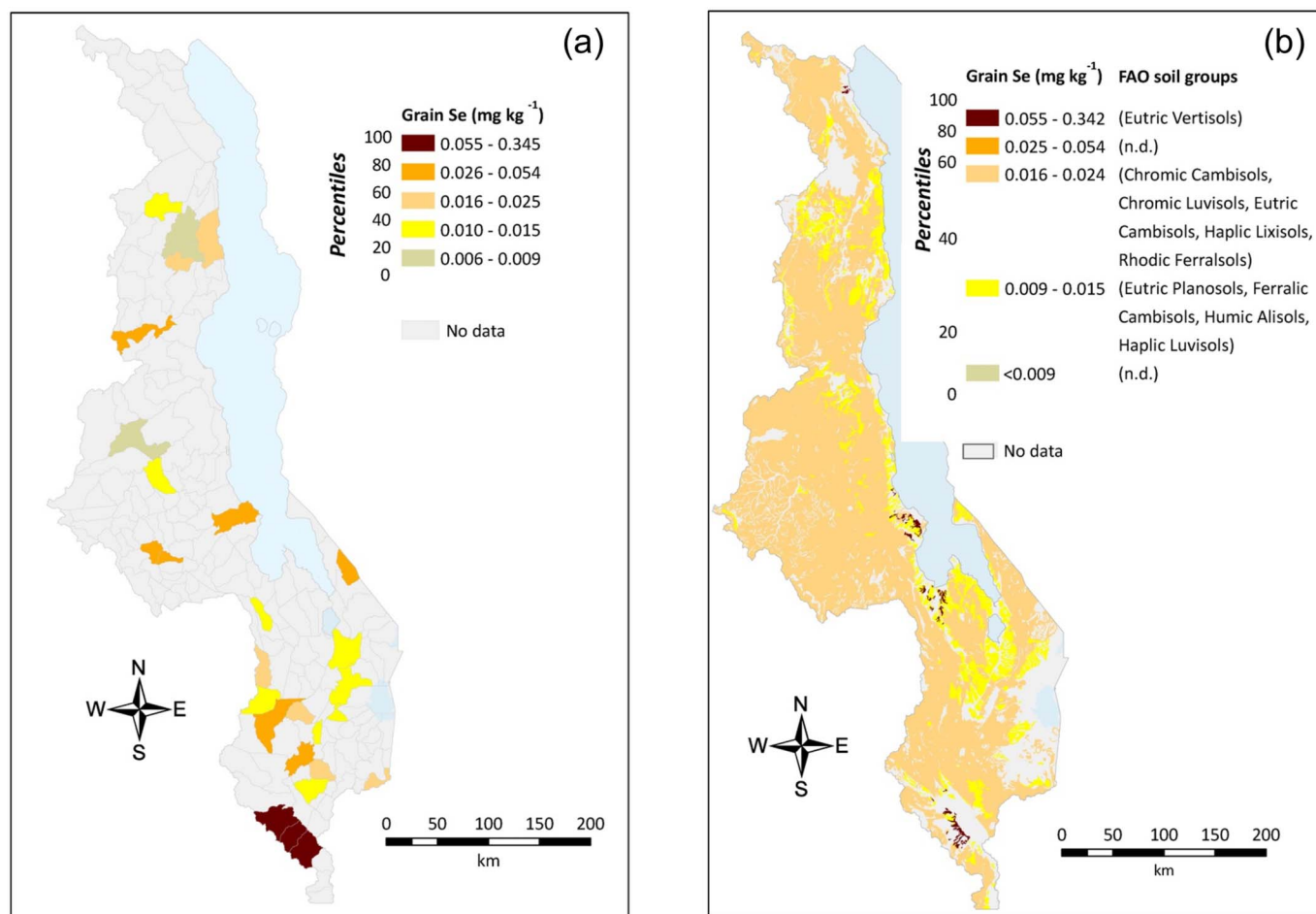
Figure 5 | (a) Median grain Se concentrations on an Extension Planning Area (EPA) basis, (b) extrapolated grain Se concentration, based on median grain Se concentration for each soil type (two quintiles of grain Se concentration are not represented by median values for each soil type; these are labelled as n.d. in the inset key). Figure produced using ArcGIS (v. 9.3).

these data were reported on both fresh and dry weight bases. Whilst both studies reported Se concentrations for fish, neither reported data for other meat products. Therefore, Se concentration data for minced meat (beef, pork, lamb) and whole-meat (chicken) products were used from UK food composition tables[33].

Selecting sites for maize and soil sampling. A non-structured sampling strategy was adopted based on extension planning systems in Malawi. This approach provided representative spatial coverage of maize grain and soil types for the major crop production areas. The national extension system comprises Agricultural Development Divisions (ADDs; n=8), Districts (n=28), Extension Planning Areas (EPAs; n=195) and Sections (n=~2,300). The first round of sampling was undertaken in May 2009 at 73 sites within 27 EPAs, representing seven of the eight ADDs. Six of these sites were under standard maize cultivation at Research Stations in Blantyre, Lilongwe, Machinga, Mzuzu, Salima and Shire Valley ADDs. The remaining 67 sites were selected as farmers' fields representing the major soil types used for maize production. Based on the high Se concentrations in maize grain from a single site in the Shire Valley ADD (Mikalango EPA) sampled in 2009, a further 15 field sites were sampled in the Shire Valley ADD in 2010 within three EPAs (Dolo, Magoti and Mikalango). The locations of sample sites are presented in Figure 1.

Collecting maize grain and soil samples. For each of the selected fields (typically 1–2 ha), eight whole maize cobs and corresponding soils were sampled from the tops of planting ridges and pooled to produce composite samples of grain and soil. A 'W' transect was used across the field, with samples collected at the top and bottom of the outer legs and at the four line mid-points of the 'W'. Whole cobs were harvested when ripe and transported to Chitedze Research Station, where they were shelled, and oven-dried to 13% moisture at 66°C and milled. Soil was sampled using a handheld soil auger to a depth of 0.15 m. Composite soil samples were transported to Chitedze Research Station where they were air dried and sieved to ≤2 mm.

Maize grain Se analysis. Milled grain (~0.4 g dry weight, DW) was digested under microwave heating for 45 min at a controlled pressure of 20 bar in 3.0 mL of 70% trace analysis grade (TAG) HNO_3, 2.0 mL H_2O_2 and 3.0 mL milli-Q water (Fisher Scientific UK Ltd, Loughborough, Leicestershire, UK). The microwave system

comprised a Multiwave 3000 platform with a 48-vessel 48MF50 rotor (Anton Paar GmbH, Graz, Austria). Samples were digested in vessels comprising perfluoroalkoxy (PFA) liner material and polyethylethylketone (PEEK) pressure jackets (Anton Paar GmbH). Digested samples were diluted to 20 mL (30% HNO_3) with milli-Q water (18.2 MΩ cm) and stored at room temperature pending elemental analysis. Immediately prior to analysis, samples were diluted 1-in-10 with milli-Q water. Selenium (^{78}Se) analysis was undertaken using ICP-MS (X-Series^{II}, Thermo Fisher Scientific Inc., Waltham, MA, USA) using a hydrogen reaction cell. Samples were introduced from a covered autosampler (Cetac ASX-520, Omaha, NE, USA) with 4 x 60-place sample racks, at 1 mL min^{-1} through a concentric glass venturi nebuliser and Peltier-cooled (3°C) spray chamber (Thermo Fisher Scientific Inc.). Internal standards were introduced to the sample stream via a T-piece and included Sc (50 ng mL^{-1}), Rh (10 ng mL^{-1}) and Ir (5 ng mL^{-1}) in 2% TAG HNO_3. An external wheat flour standard (NIST 1567a; National Institute of Standards and Technology, Gaithersburg, MD, USA) was used as reference material. Each digestion batch (n=48) included two blank digestions; final Se concentrations were converted to mg kg^{-1} DW.

Soil analyses (total Se, KH_2PO_4-extractable Se, and other soil properties). For total Se analyses, sieved soil (~0.2 g DW) was fully digested in 70% HF, 70% HNO_3 and 60% $HClO_4$ (TAG; Fisher Scientific UK Ltd), using PFA digestion vessels and a 48-place teflon-coated graphite block digestor (Model A3, Analysco Ltd, Chipping Norton, UK). Digested samples were diluted to 50 mL using milli-Q water and stored in 5% HNO_3 at room temperature in universal sample bottles pending elemental analysis. Most samples were analysed in triplicate and an estuarine sediment (NIST 1646a, NIST) was used as an external standard reference material. For extractable Se analyses, the method of Zhao and McGrath[34] was used. Triplicate samples of air-dried sieved soil (10 g) were shaken with 30 mL 0.016 M KH_2PO_4 (pH 4.8) in polycarbonate centrifuge tubes for 1 h. Soil suspensions were then centrifuged for 20 min at 2200 rpm, filtered to <0.22 μm using a Millex syringe driven filter unit (Millipore, Cork, Ireland) and stored at room temperature prior to analysis for Se by ICP-MS, as described previously. Other soil properties measured included soil pH in water, texture using the hydrometer method[35], and organic carbon using an adapted chromic acid titration method[36].

7

Table 2 | Median Se intake from maize at a District level in Malawi, based on distributions of population and soil type, integrated with median grain Se concentrations from each soil type

District		Population[a] (k)	Area represented by FAO soil type (km²)[b]										Other soils	Total area (km²)	Median Se intake from maize (µg person⁻¹ d⁻¹)[c]
			Chromic Cambisols	Chromic Luvisols	Eutric Cambisols	Eutric Planosols	Eutric Vertisols	Ferralic Cambisols	Haplic Lixisols	Haplic Luvisols	Humic Alisols	Rhodic Ferralsols			
1	Balaka	317	-	520	326	265	-	-	-	773	-	-	272	2155	5.3
2	Blantyre	999	259	321	1150	11	-	-	72	4	-	-	200	2017	5.2
3	Chikwawa	439	-	283	2002	-	188	-	-	287	-	-	2123	4883	13.1
4	Chiradzulu	291	79	328	159	-	-	-	-	15	-	-	165	748	5.4
5	Chitipa	179	32	329	184	-	-	147	2566	21	-	-	970	4248	7.3
6	Dedza	624	-	2223	583	50	32	-	68	138	-	-	684	3777	6.8
7	Dowa	557	6	2296	180	-	-	72	48	37	-	-	228	2868	5.7
8	Karonga	273	55	59	871	-	25	14	1291	33	-	-	1094	3441	7.8
9	Kasungu	616	-	2141	21	-	-	111	5088	-	-	-	702	8064	7.2
10	Likoma	10	-	-	-	-	-	-	-	-	-	-	-	-	-
11	Lilongwe	1897	-	4750	630	-	-	3	271	-	-	-	500	6154	5.7
12	Machinga	489	41	147	513	242	-	-	252	555	-	-	2110	3860	5.5
13	Mangochi	804	-	579	1971	232	44	-	1361	1187	-	-	1037	6409	6.8
14	Mchinji	457	-	1461	33	-	-	68	1007	-	-	-	576	3145	6.5
15	Mulanje	525	18	35	88	-	-	-	223	17	112	299	1104	1895	6.3
16	Mwanza	94	89	755	1130	-	-	-	145	14	-	-	192	2326	5.5
17	Mzimba	853	101	553	83	-	-	1055	6574	214	-	347	1546	10474	7.2
18	Neno	109	-	-	-	-	-	-	-	-	-	-	-	-	-
19	Nkhata Bay	214	-	-	6	-	-	995	1926	-	-	668	759	4354	6.8
20	Nkhotakota	302	231	743	383	-	4	224	1668	391	-	83	591	4318	6.6
21	Nsanje	238	-	236	743	-	1	-	-	167	-	-	822	1969	5.3
22	Ntcheu	474	-	1304	973	37	47	93	87	235	-	-	562	3246	7.5
23	Ntchisi	224	-	1016	46	-	-	-	748	-	-	-	34	1938	6.5
24	Phalombe	313	8	-	205	-	-	-	51	-	9	-	1276	1549	5.5
25	Rumphi	169	39	-	83	-	-	994	1597	-	-	40	1830	4584	6.7
26	Salima	340	-	350	183	-	133	2	433	375	-	-	637	2113	16.6
27	Thyolo	587	371	399	174	-	-	-	212	-	323	116	75	1669	5.6
28	Zomba	671	16	719	306	21	-	-	-	337	41	-	1730	3170	5.5
	residual	-	-	1	1	-	-	-	3	-	-	-	3	8	-
	Totals	13065	1346	21546	13026	859	473	3778	25691	4801	486	1553	21821	95380	
Grain Se (mg kg⁻¹)	lower 25%		0.009	0.009	0.009	0.010	0.254	0.009	0.009	0.009	-	0.006			
	median		0.014	0.016	0.014	-	0.342	0.014	0.022	0.016	0.013	0.018			
	upper 25%		0.030	0.028	0.030	-	0.356	0.030	0.042	0.028	-	0.021			

[a] based on NSO (2008; ref. 37)
[b] based on Green and Nanthanbwe (1992; ref. 24)
[c] based on 354 g maize person⁻¹ d⁻¹ (FAO, 2011; ref 15); assumes equal population distribution within a district; excludes maize grain production on "other soils"

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Author contributions

ADCC, SDY, CRB, JL and MRB conceived the study and designed the experiments. ADCC collected the samples; ADCC, SDY and KBR analysed the samples. ADCC, SDY, ELA, MJW and MRB conducted data analysis. All authors were involved in drafting and reviewing the manuscript and figures.

Additional information

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